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# Dynamic Mechanical Thermal Analysis of Wood Modified with Bio-Polyesters

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## ABSTRACT

Chemical modification of wood with bio-polyesters, namely polylactic acid (PLA) and polybutylene succinate (PBS), has recently been reported (Noël *et al.* 2015, Grosse *et al.* 2017a). Both oligomeric treatments (OBS and OLA) confer interesting properties to wood for outdoor applications. They are based on the impregnation of oligomers in oven-dried beech wood (*Fagus sylvatica* L.), followed by a curing step at 100 or 120°C for OBS or 160°C for OLA. Unlike treatment with OLA, the dry curing conditions did not allow any penetration of OBS in wood cell walls, thus no gain in anti-swelling efficiency (ASE) was seen. Humid treatment conditions were observed to allow a partial diffusion of OBS in cell walls, most likely because of water acting as swelling agent. Hydro-thermal treatment (HTT) was carried out at several temperatures, relative humidities and durations, to find optimal conditions of OBS diffusion in the wood structure. Treatment conferred ASE of 60% to 70%, with a good correlation to OBS diffusion. (Grosse *et al*. 2017b). In this study, dynamic mechanical thermal analysis (DMTA) under varying humidity was carried on for understanding OBS/OLA interactions with wood polymers. First, temperature scans were performed from -150°C to 150°C at a heating rate of 5 °C/min and for a frequency of 1, 10 and 100 Hz. Glass transitions of wood components and oligomers appeared in the tan δ response of the modified wood. In a second set of experiments the relative humidity in the chamber was set at 35% and the temperature changes were manually performed when the conditions in the chamber were stable. Wood impregnated with OBS but not hydrothermally-treated has the same behaviour as untreated wood, indicating few interactions between the polymer and the cell walls. This is well correlated with the low diffusion of OBS into wood structure. In the case of hydrothermally-treated samples the same global behaviour can be observed. In the case of OLA treated wood, the stiffness of the material decreases more rapidly with the temperature, in comparison with the OBS treated wood. Oligomers of lactic acid, more hydrophilic and smaller than the PBS ones, are more likely diffusing then interacting with the cell walls polymers.

## INTRODUCTION

As a renewable material, wood has many advantageous properties such as workability, mechanical strength, sustainability and pleasant aesthetic features. However, wood is sensitive to its environment, especially regarding moisture. Due to its chemical composition, the dimensional stability against humidity and biological resistance of wood are limited. Chemical modification of wood with polybutylene succinate (PBS) has been reported to confer interesting properties to wood for outdoor applications (Noël *et al.* 2015a, 2015b, Vitkeviciute *et al.* 2014). This treatment was based on the hot impregnation (90°C) of PBS in oven-dried beech wood (*Fagus sylvatica* L.), followed by a curing step at 100/120°C for 6h/96h. The dry treatment conditions did not allow any penetration of the oligomers in wood cell walls, thus any anti-swelling efficiency (ASE). The mechanical properties were not influenced either. However, the PBS lumen-filling led to a substantial decrease in wood hygroscopicity. Moreover, a good retention of oligomers into the wood lumens was observed, with ca. 80% retention rate of the impregnated polymers in wood during water leaching. Humid treatment conditions were observed to allow a partial diffusion of the oligomers into the cell walls, most likely because of water acting as swelling agent inducing partial penetration of oligomers in the cell wall. Humid treatment conferred anti-swelling efficiency (ASE) of 60% to 70%, with a good correlation to PBS diffusion. This phenomenon is not yet fully understood. For that reason, the dynamic mechanical thermal analysis (DMTA) under varying humidity is expected to help the understanding. Hydro-thermal treatment (HTT) was carried out at several temperatures, relative humidity and duration, in order to find optimal conditions of PBS diffusion into the wood structure. Most effective HTT to carry out for eventual up-scaling is to be determined: low temperature for long time, or short time at high temperature. The question of wood components degradation might be decisive. DMTA under varying humidity is expected to help the selection of the best option through analyse of the influence of treatment parameters (temperature, relative humidity and duration) on wood/oligomers interactions.

## EXPERIMENTAL

### *Samples preparation*

Samples were prepared as described by Noël *et al*. (2015b). Oven-dried wood samples were immersed in liquid oligomers, OBS, OLA L and OLA S respectively, at 90°C, 60°C and 20°C respectively. Containers were then placed in a vacuum oven under reduced pressure (150 mbar) for 20 to 30 min, then atmospheric pressure over 20 to 30 min. Impregnated samples were then wiped.

Weight uptake (WUi) and swelling (Si) after impregnation have been calculated as follows:

$$WU_i\ (\%) = \frac{w_i - w_{u,d}}{w_{u,d}} \times 100 \quad (1)$$

$$S_i\ (\%) = \frac{V_i - V_{u,d}}{V_{u,d}} \times 100 \quad (2)$$

where $w_i$ and $V_i$ stand for the impregnated sample weight and volume respectively and $w_{u,d}$ and $V_{u,d}$ for the sample untreated anhydrous weight and volume.

For the OBS-treated samples, the following HTT was carried out in a pressurized reactor at 100% relative humidity (RH) and different temperatures for different durations. For all samples, a final thermal post-treatment (PT) was carried out to dry the treated samples and was expected to partially cure and fix the oligomers in wood. Table 1 summarises the treatments conditions.

Weight uptake (WUt) and swelling (St) after treatment were calculated as follows:

$$WU_t\ (\%) = \frac{w_{t,d} - w_{u,d}}{w_{u,d}} \times 100 \quad (3)$$

$$S_t\ (\%) = \frac{V_{t,d} - V_{u,d}}{V_{u,d}} \times 100 \quad (4)$$

where $w_{t,d}$ and $V_{t,d}$, and $w_{u,d}$ and $V_{u,d}$ respectively stand for treated and untreated samples anhydrous weight and volume respectively. All samples were then stabilised at 35% RH.

***Table 1: description of treatments conditions***

| Sample | Impregnation product | Hygro-thermal treatment | | | Post treatment | |
|---|---|---|---|---|---|---|
| | | Temperature [°C] | RH [%] | Duration [h] | Temperature [°C] | Duration [h] |
| **PBS A** | PBS | 100 | 100 | 2 | 103 | 72 |
| **PBS B** | | | | | 120 | 72 |
| **PBS C** | | 130 | 100 | 0.5 | 103 | 72 |
| **PBS D** | | | | | 120 | 72 |
| **PBS E** | | 160 | 100 | 0.5 | 103 | 72 |
| **PBS F** | | | | | 120 | 72 |
| **PBS G** | | - | - | - | 103 | 72 |
| **PBS H** | | - | - | - | 120 | 72 |
| **OLA S** | Short OLA | - | - | - | 160 | 48 |
| **OLA L** | Long OLA | - | - | - | 160 | 48 |
| **REF** | None | - | - | - | - | - |

### *Dynamic mechanical analysis*

First, the dynamic mechanical thermal analysis (DMTA) has been carried out on a Triton TTDMA. Temperature scans were performed from -150°C to 150°C at a heating rate of 5 °C/min and for a frequency of 1, 10 and 100 Hz.

A second DMA analysis has been then carried out using a humidity generator connected to the Triton TTDMA, to allow a temperature ramp while controlling the RH in the chamber. Samples of dimensions 50×10×4mm (L×RT×TR) were used in both sets of experiments. RH was set at 35% and the temperature changes were manually performed when the conditions in the chamber were stable. Once the temperature and RH were stable, the average of five values of the stabilised storage modulus was calculated. Only relative storage modulus values and tan delta for 1Hz are reported.

## RESULTS AND DISCUSSION

### *Dynamic mechanical thermal analysis (DMTA)*

Table 2 summarises samples weight and volumetric variations during treatment. After impregnation, both polymers mostly remain in the cell lumens according to the low $S_i$. With heating, there is a product migration into the wood structure. $S_t$ is most likely due to product diffusion in the cell walls. For PBS, diffusion is more effective with HTT than with only PT and for OLA, a PT carried out at 160°C is sufficient.

***Table 2: Samples weight variations (WUi and WUt) and volumetric variations (Si and St) after impregnation and after treatment (only the data of the one sample used for DMTA are presented).***

| | WUi [%] | WUt [%] | Si [%] | St [%] |
|---|---|---|---|---|
| **PBS B** | 86.9 | 77.5 | 0.5 | 15.1 |
| **PBS D** | 88.7 | 80.2 | 1.8 | 13.7 |
| **PBS F** | 82.4 | 66.1 | 2.6 | 12.8 |
| **PBS H** | 79.1 | 75.1 | 1.8 | 7.6 |
| **OLA S** | 62.7 | 29.9 | 0.4 | 12.1 |
| **OLA L** | 81.8 | 51.1 | -0.5 | 16.3 |

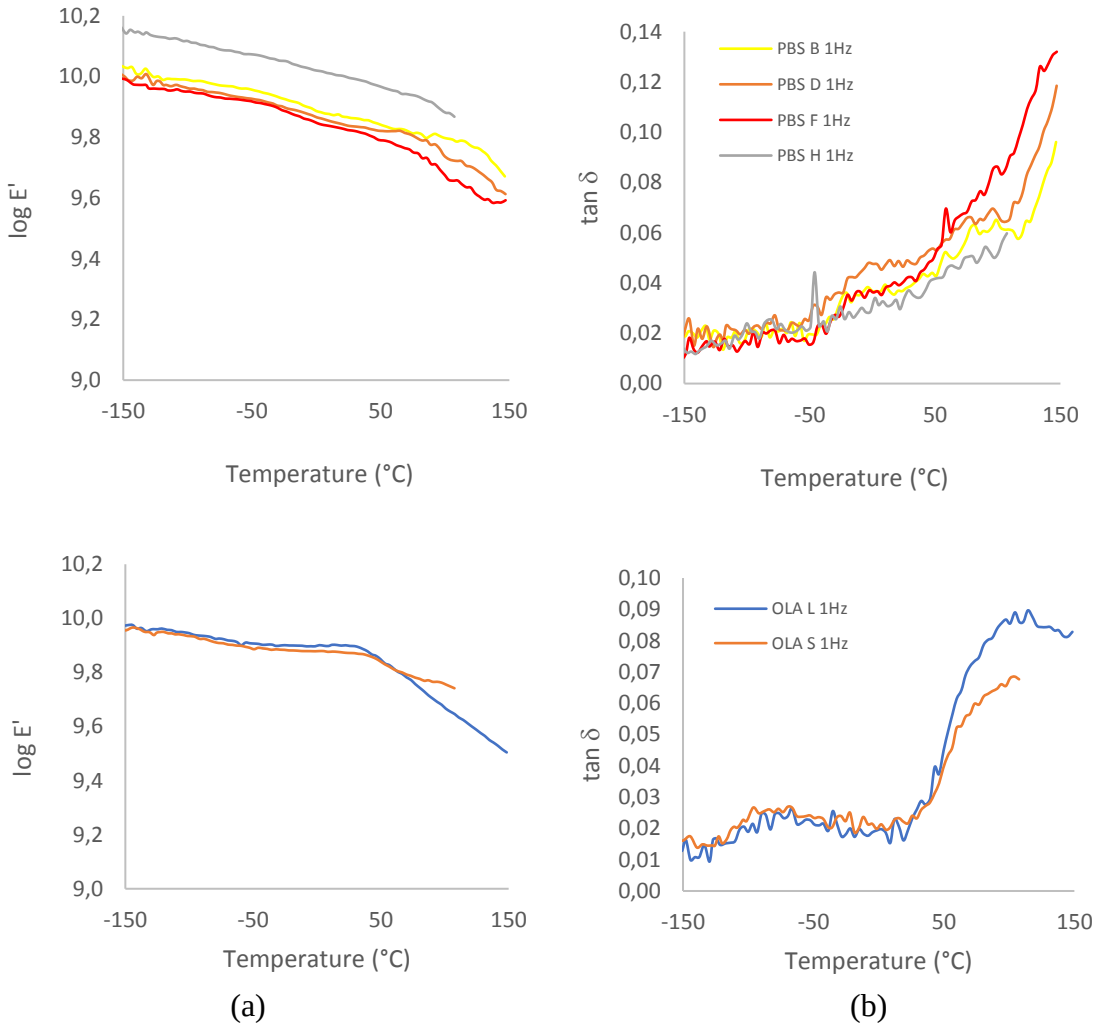


***Figure 1: Effect of polymers on the dynamic mechanical response (a) log E' and (b) tan δ for a frequency of 1Hz.***

Wood DMTA has been widely studied. The tan δ response of untreated wood usually shows a low temperature transition (β) at between -90 and -110 °C, and a broad transition (α1) centred around 80 to 100°C with a shoulder (α2) between 10 and 60°C (Kelley *et al*. 1987). Glass transition temperature ($T_g$) of PBS and PLA respectively is around -45 to -50 °C and around 40 to 60°C respectively. As oligomers present in the modified wood are smaller than industrial polymers, those transitions might appear in the lower range of temperature in the tan δ response of the modified wood (Figure 1).

For PBS treated wood, the tan δ response is very similar to untreated wood. However, the β transition is not clear and α1 transition might have been shifted to slightly higher temperature, showing a reduced amount of small molecules in wood structure and reduced mobility of cell walls components. A transition around -50 °C appears in the tan δ response of PBS H but not in the others. It might just be a measurement error or it can be the $T_g$ of PBS from the lumens as it is the only variant not submitted to hydrothermal treatment. For OLA treated wood, the β transition is visible around -80 °C and α1 is broader than for untreated wood. α1 transition is most likely due to both wood and OLA as the PLA $T_g$ is around 40 to 60 °C.

### *Effect of PBS on the dynamic mechanical response at 35% RH*

Table 3 summarise samples weight and volumetric variation during treatment. First, one sample for each variant was run on the DMA after stabilisation in a desiccator at 35% RH. At this RH, treated samples were very dry as they all had an EMC below 2%. Figure 2 and Figure 3 show the relative storage modulus (E') and tan δ response for this first batch of samples. The reference sample (REF) relative E' is slightly increasing (about 5%) with the temperature from 20 to 30 °C and is then decreasing back to its original value at 20°C. Wood impregnated with PBS but not hydrothermo-treated (PBS G) has the same behaviour indicating few interactions between the polymer and the cell walls. This is well correlated with the low diffusion of PBS into wood structure ($S_t$ = 3.1%). Impregnation followed by heat treatment at 120°C allows to double the wood swelling after treatment (PBS H). Relative E' is increasing with the temperature but seems to stabilise instead of decrease. In the case of samples impregnated with PBS and then treated with hydrothermal treatment and post-treatment (PBS A, B, E, and F), the same behaviour can be observed. Relative E' is decreasing with temperature. However, some variants ran a second time, with another sample, showed opposite behaviour, like PBS A (Figure 4). Information provided is not fully understood yet, but reproducibility of the experiment is uncertain. Thus, several replicates are currently on going to validate the results and understand the reasons of such variability.

***Table 3: Samples weight variations (WUi and WUt) and volumetric variations (Si and St) after impregnation and after treatment (only the data of the one sample used for DMTA are presented).***

| | **WUi [%]** | **WUt [%]** | **Si [%]** | **St [%]** |
|---|---|---|---|---|
| **PBS A3** | 80.7 | 74.6 | -0.4 | 14.9 |
| **PBS A2** | 90.5 | 84.6 | 0.1 | 15.8 |
| **PBS B** | 85.8 | 78.6 | 1.2 | 15.4 |
| **PBS E** | 86.8 | 72.2 | 2.4 | 13.9 |
| **PBS F** | 86.2 | 69.1 | 4.4 | 13.1 |
| **PBS G** | 77.9 | 75.8 | 0.3 | 3.1 |
| **PBS H** | 80.1 | 76.6 | 1.0 | 7.4 |
| **REF** | - | - | - | - |

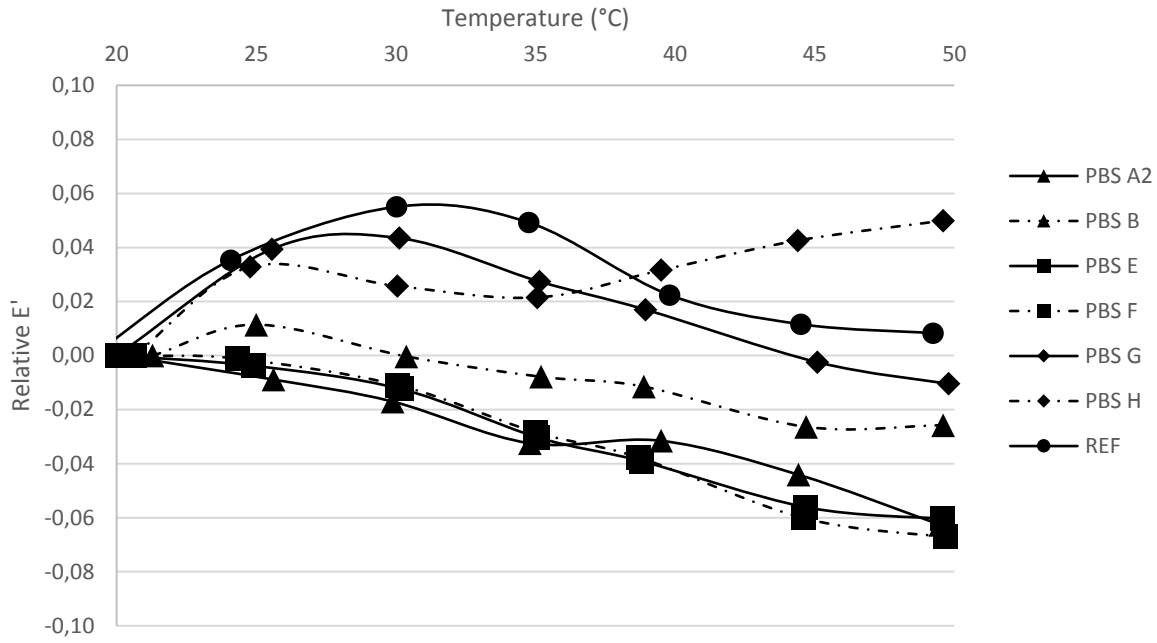


***Figure 2: Effect of PBS on the dynamic mechanical response regarding relative E' for a frequency of 1Hz.***

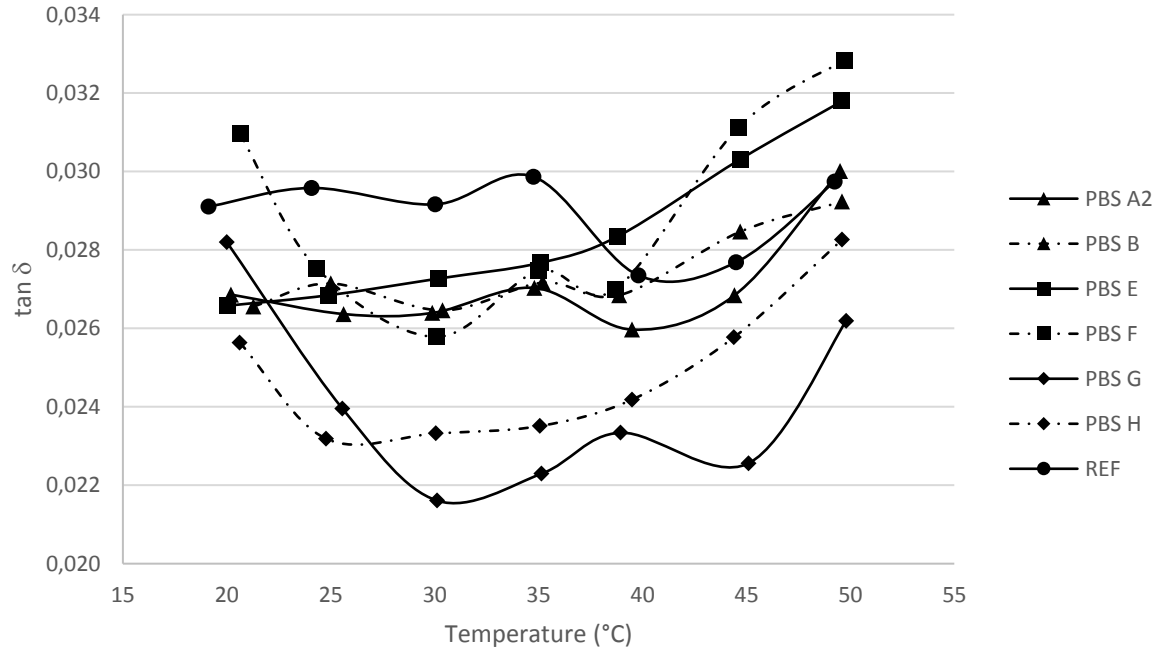


***Figure 3: Effect of PBS on the dynamic mechanical response regarding tan δ for a frequency of 1Hz.***

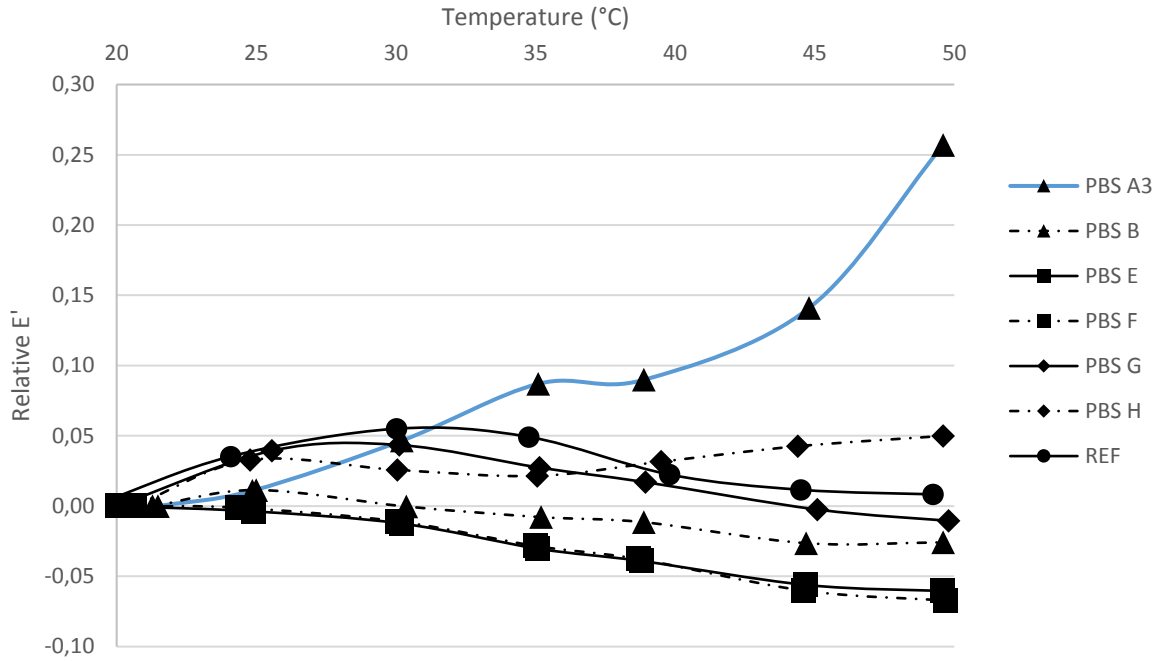


***Figure 4: Effect of PBS on the dynamic mechanical response regarding relative E' for a frequency of 1Hz.***

## *Effect of OLA on the dynamic mechanical response at 35% RH*

In the case of OLA treated wood, the stiffness of the material decreases more rapidly with the temperature in comparison with the PBS treated wood. Oligomers of lactic acid, more hydrophilic and smaller than the PBS ones, are more likely diffusing then interacting with the cell walls polymers.

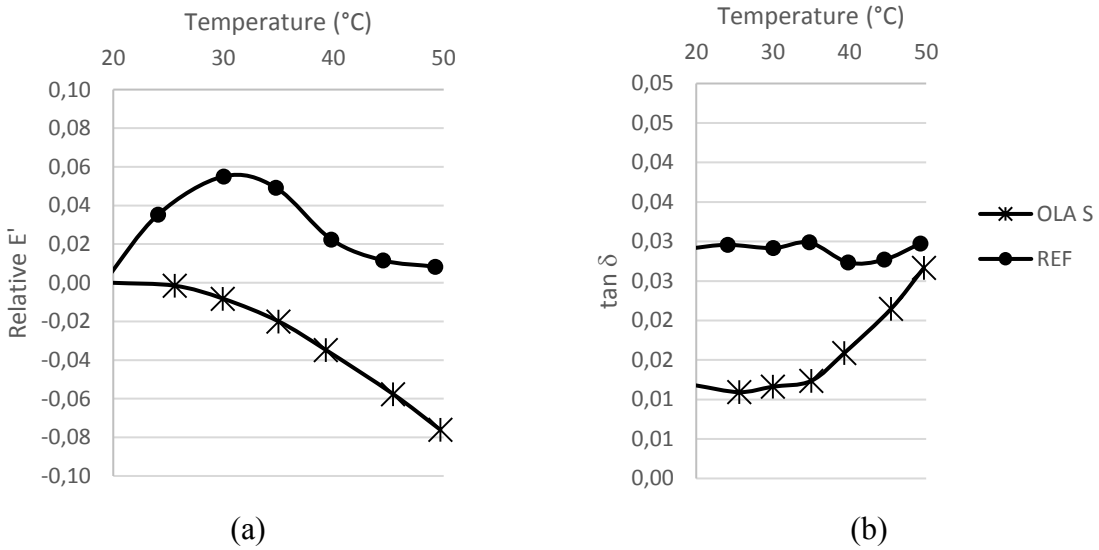


***Figure 5: Effect of OLA on the dynamic mechanical response regarding (a) relative E' and (b) tan δ for a frequency of 1Hz.***

## CONCLUSIONS

As conclusion, the DMA provided interesting pre-results and revealed to be a possible way to investigate the influence of hydrothermal treatment and post-treatment conditions on the mechanical properties, as well as on the interaction of wood with the polymer. However, more experiments are still on going to reinforce the analyse and the results.

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